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Published in:
Macromolecules

DOI:
[10.1021/ma951203o](https://doi.org/10.1021/ma951203o)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1996

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Teerenstra, M. N., Klap, R. D., Bijl, M. J., Schouten, A. J., Nolte, R. J. M., Verbiest, T., & Persoons, A. (1996). Preparation of Langmuir-Blodgett mono- and multilayers of copolymers of isocyanides with NLO-active side chains. Effect of a spacer group between the NLO chromophore and the polymer backbone. *Macromolecules*, 29(14), 4871 - 4875. <https://doi.org/10.1021/ma951203o>

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Preparation of Langmuir–Blodgett Mono- and Multilayers of Copolymers of Isocyanides with NLO-Active Side Chains. Effect of a Spacer Group between the NLO Chromophore and the Polymer Backbone

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Received August 17, 1995; Revised Manuscript Received April 25, 1996[®]

ABSTRACT: The structure and properties of Langmuir–Blodgett films of copolymers of a hydrophilic isocyanide and an isocyanide containing an NLO-active moiety with a spacer group are studied. Depending on the ratio of the two monomers, the copolymers are able to form stable monolayer films. The orientations of the NLO groups in the copolymers with respect to the film plane have been derived from polarized transmission and grazing incidence reflection (GIR) IR spectra. Quantitative analysis of the spectra shows that the polymer main chains have no specific orientation in the plane of the film. The side chains of copolymers with a high NLO-dye content appear to be oriented perpendicular to the film plane.

Introduction

Some 20 years ago it was recognized that Langmuir–Blodgett (LB) films may be interesting materials for applications in the areas of optoelectronics, microelectronics, and molecular electronics.^{1–3} Since that time much research has been focused on the preparation of LB films from low molecular weight amphiphiles. Such films are, however, very fragile and unlikely to be suitable for commercial devices. Moreover, it has been demonstrated recently that both during⁴ and after⁵ their deposition LB multilayers may become disordered. These problems are likely to be less serious if the LB films are prepared from preformed polymers, and this has led to a series of extensive studies by different research groups.^{6–9} Of particular interest in this connection are polymers with nonlinear optical (NLO) moieties, which may be used to construct electrooptical devices. NLO moieties covalently linked to a polymer do not lead to phase separation, which is a problem when the NLO molecule is mixed with a polymer matrix. Consequently, a high load of NLO-active chromophores can be used.^{10,11} Moreover, by tethering the NLO phore to a polymer backbone a greater long-term stability of the NLO response may be expected. However, if relaxation can occur due to unfavorable dipole–dipole interactions, the stability of the $\chi^{(2)}$ activity may still be low. The covalent bond between the NLO phore and the polymer backbone can help restrict some of the relaxation modes. However, most polymers currently used to anchor NLO functions possess poor thermal properties (polystyrene, PMMA). This results in relaxations in the matrix which are still too rapid for useful device applications.

Electric field poling at, or above, the glass transition temperature T_g is the most common method to introduce macroscopic polar order into a polymer film. Long-term stability of the poled state is very important for future applications. Macroscopic ordering of systems with chromophores covalently bound to a flexible polymer backbone has been the subject of extensive investigations and has been comprehensively reviewed by Staring.¹²

In this study polymers are investigated containing azobenzene-based chromophores which are linked to the rigid backbone of a poly(isocyanide) via hydrocarbon spacers. The spacer groups have been incorporated for two reasons. First, they result in the chromophores being more or less detached from the rigid backbone. This should facilitate the orientation of these functions, which may lead to monolayers and LB films with a higher NLO activity. Second, the spacer groups allow the hydrophilic ester groups, located near the backbone of the polymers, to become more accessible to the water surface, which facilitates the formation of H-bonds as compared to the polymers without a spacer group.¹³ In the latter polymers the ester functions were more or less shielded from the water surface by the large hydrophobic dye fragments.

Experimental Section

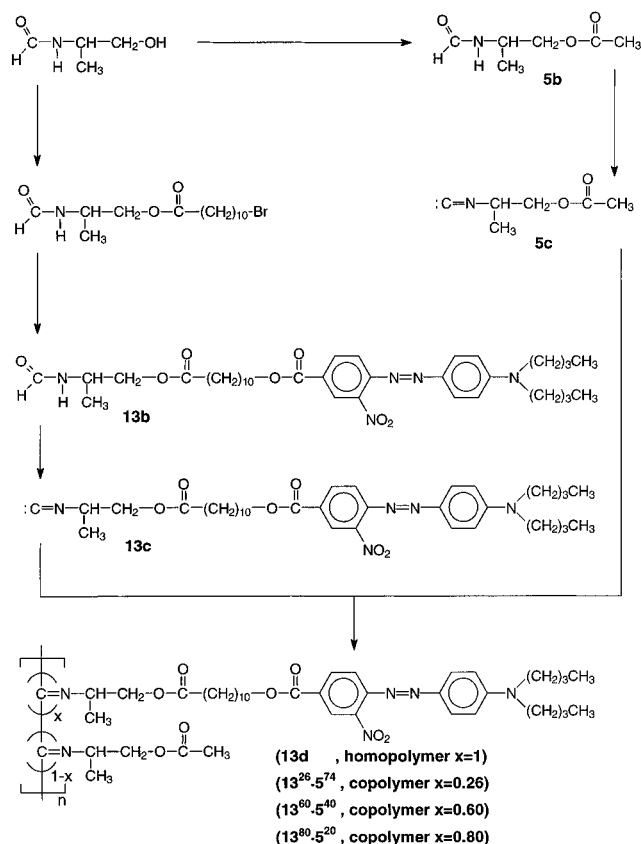
Materials. The route which is used to synthesize the polymers in this study is given in Scheme 1. A detailed description of the procedures is available on request in the supporting information.

Techniques. The equipment and the procedures used to study monolayers, prepare LB films, and perform IR measurements was described earlier by us.¹⁴

Ellipsometry. Film thicknesses were measured using a Gaertner L117-c or L117 production ellipsometer at a wavelength of 632.8 nm as well as with a homebuilt spectrometer. The latter was an automated four-zone ellipsometer¹⁵ with a

[®] Abstract published in *Advance ACS Abstracts*, June 15, 1996.

Scheme 1



spectral range between 214 and 2300 nm and a resolution of 0.01 nm (typically chosen at 1 nm). The measured parameters Δ and Ψ had a relative accuracy of 2×10^{-4} and an absolute reproducibility of 10^{-3} deg. Refractive indices of the multilayered films were determined at chosen wavelengths (typically 532, 632.8, and 1064 nm).

NLO Measurements. The NLO activity of floating Langmuir layers was determined by measuring the generated second-harmonic intensity using the setup described by S'heeren et al.¹⁶ Using silver as a reference¹⁷ one can obtain values for the nonlinearity of the layer. The use of polarizers in the fundamental and reflected beam offers the possibility to determine the different components of the second-order susceptibility tensor $\chi^{(2)}$.

The NLO activity of LB films was determined by measuring the second-harmonic intensity generated from multilayered samples on glass substrates, using the setup described by Cnossen et al.¹⁸ The second-harmonic intensity was referenced to a clean silver mirror (100% reflectance) with $\chi^{(2)} = 1.3 \times 10^{-9}$ esu (at $p_{\text{incidence}} - p_{\text{detection}}$ polarization setting).¹⁹ For conversion into SI units one can use, in the case of β , the relationship $1 \text{ Cm}^3\text{V}^{-2} = 2.7 \times 10^{20}$ esu and, in the case of $\chi^{(2)}$, $1 \text{ CV}^{-2} = 2.7 \times 10^{14}$ esu.

Results and Discussion

Monolayer Behavior and Transfer. In Figure 1 different pressure–area isotherms of polymer **13d** are shown. Attempts to form stable films of this polymer, at various surface pressures, were not successful. Transmission electron microscopy revealed that the floating films of polymer **13d** consisted of rather thick domains or droplets (Figure 2a). A TEM micrograph, shown in Figure 2b, revealed that the polymer film consisted of different thin layers on top of each other.

To obtain polymers with improved film-forming properties, three copolymers were synthesized with different dye contents (see Experimental Section). Pressure–area isotherms of polymer **13²⁶.5⁷⁴**, a copolymer with

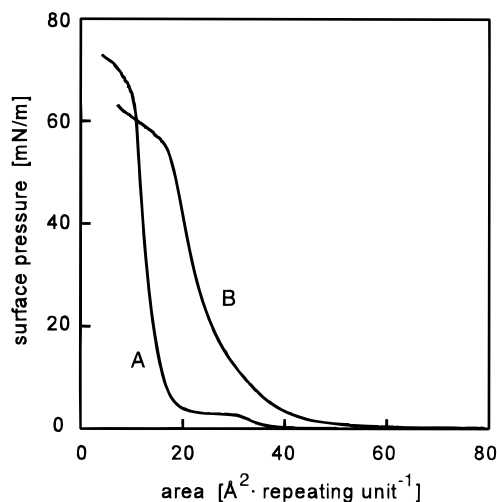


Figure 1. Pressure–area isotherms of polymer **13d**. Compression started at (A) 1 h and (B) 24 h after film spreading.

26 mol % of dye fragments, clearly showed the presence of a plateau which was reached at a lower pressure when the temperature was increased. The specific area, A_0 , was found to be 30 Å^2 per repeating unit (Figure 3). Taking into account that 74% of the polymer consists of repeating units which occupy an area of 17 Å^2 per unit,¹⁴ this leaves an area of 68 Å^2 for each dye fragment.

The effect of the spacer groups can be seen more clearly in Figures 4 and 5, where the pressure–area isotherms of copolymer **13⁶⁰.5⁴⁰** and copolymer **13⁸⁰.5²⁰** are plotted at different temperatures.

Depending on the temperature, the pressure starts to rise between 50 and 60 Å^2 per repeating unit and continues to rise slowly until an inflection point is reached. At surface pressures lower than those of the inflection points stable films could be obtained. This was not possible at higher surface pressures, not even at very low temperatures ($T < 5^\circ \text{C}$). From the isotherms of polymer **13⁸⁰.5²⁰** at 10, 20, and 30°C a specific area A_0 of approximately 36 Å^2 per repeating unit can be derived. This means that each of the dye fragments in this polymer occupies 40 Å^2 . This value is much smaller than the one determined for polymer **13²⁶.5⁷⁴** (68 Å^2) and slightly smaller than that measured for **13⁶⁰.5⁴⁰** (44 Å^2). From these values it can be concluded that the chromophores in the copolymers with the higher dye contents are oriented more perpendicular to the water surface. Theoretically, assuming an upright orientation, the dye fragment would occupy an area of approximately 32 Å^2 .

In contrast to polymer **13d**, the three copolymers did form stable films at the air–water interface and appeared to be transferable onto various substrates. Transfer of polymer **13²⁶.5⁷⁴** was close to perfect Z-type. When the dye content was increased, as in polymers **13⁶⁰.5⁴⁰** and **13⁸⁰.5²⁰**, the transfer changed to more or less Y-type deposition.

Infrared Measurements. FT-IR measurements were carried out on the LB films to determine the orientation of the chromophores with respect to the plane of the film. Comparison of the transmission IR spectra of LB films prepared on ZnS substrates and measured with different polarizations of the IR light revealed no differences in the intensities of the absorption peaks. This was the case for all polymers investigated. We may therefore conclude that no orientation in the plane of the film is present and that alignment

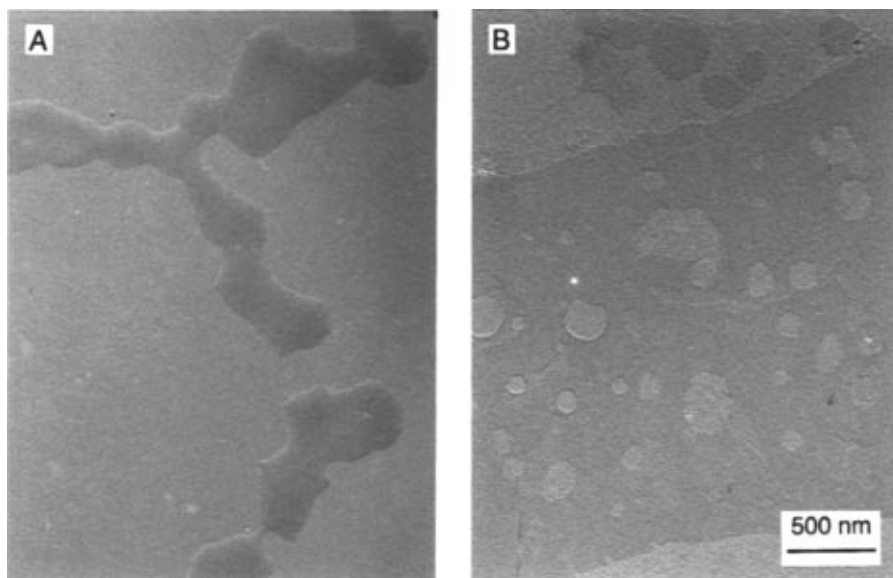


Figure 2. Transmission electron micrographs of polymer **13d** (A) directly after spreading and (B) after being left at the subphase for 24 h, at a surface pressure of 3 mN/m.

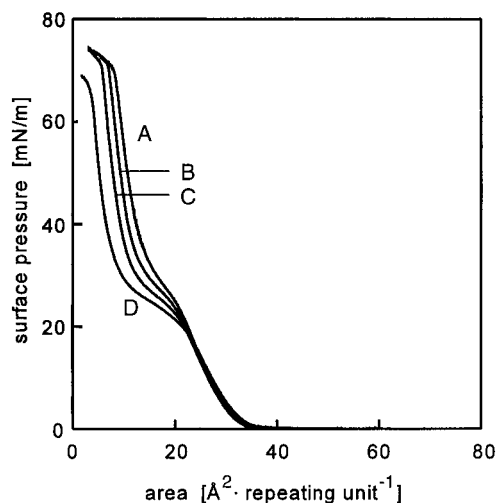


Figure 3. Pressure–area isotherms of polymer **13^{26.574}** at (A) 10 °C, (B) 20 °C, (C) 30 °C, and (D) 40 °C.

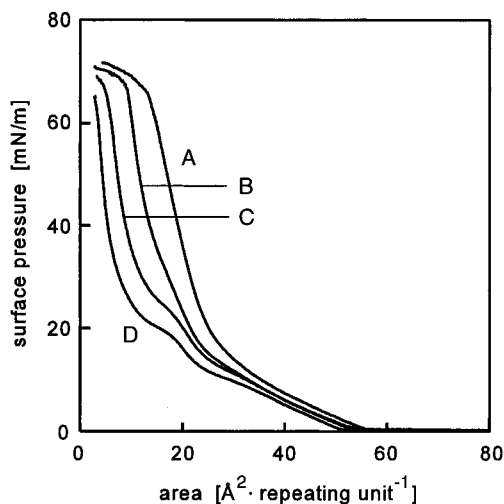


Figure 4. Pressure–area isotherms of polymer **13^{60.540}** at (A) 10 °C, (B) 20 °C, (C) 30 °C, and (D) 40 °C.

of the rigid polymer backbones due to the shear flow during the transfer process does not occur.

The transmission spectra taken from multilayers of the different copolymers were compared with the graz-

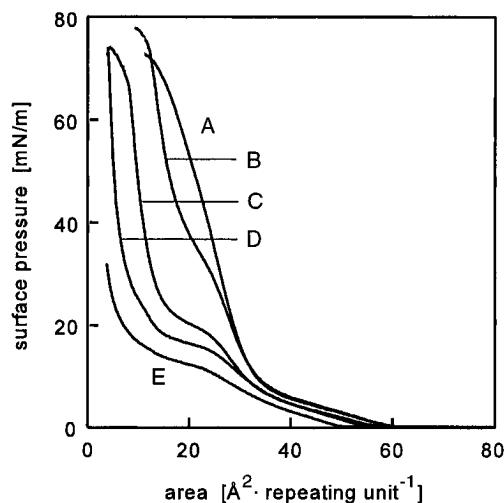


Figure 5. Pressure–area isotherms of polymer **13^{80.520}** at (A) 5 °C, (B) 10 °C, (C) 20 °C, (D) 30 °C, and (E) 40 °C.

ing incidence reflection (GIR) spectra. One can determine the preferred orientation of the chromophores by assuming a random orientation of the CH_2 groups and by comparing the intensity of the CH_2 stretch vibration ($\nu_a \text{CH}_2$), located at approximately 2929 cm^{-1} , with that of the aromatic ring vibration ($\delta \text{C}=\text{C}$) of the azobenzene chromophore located at approximately 1600 cm^{-1} . The dipole moment of the latter vibration is oriented parallel with respect to the long axis of the chromophore. This absorption was used to determine the preferred orientation of the dye fragments. The C_{10} spacer groups as well as the dibutylamino groups do not crystallize, so the assumption of random orientation of the CH_2 groups is probably valid. Thus, the ratio of the absorptions at 2929 and 1600 cm^{-1} should give a good indication on the alignment of the dye fragments in the LB films.

In Figure 6 the GIR spectra for the three copolymers are shown. The ratio of the absorptions, $\delta(\text{C}=\text{C})/\nu_a(\text{CH}_2)$, is 1.3, 2.5, and 3.0 for **13^{26.574}**, **13^{60.540}**, and **13^{80.520}**, respectively. From these values it can be concluded that the azobenzene chromophores in polymer **13^{60.540}** are oriented more perpendicular to the plane of the LB film than those in polymer **13^{26.574}**. LB films of polymer **13^{80.520}** show an even better molecular

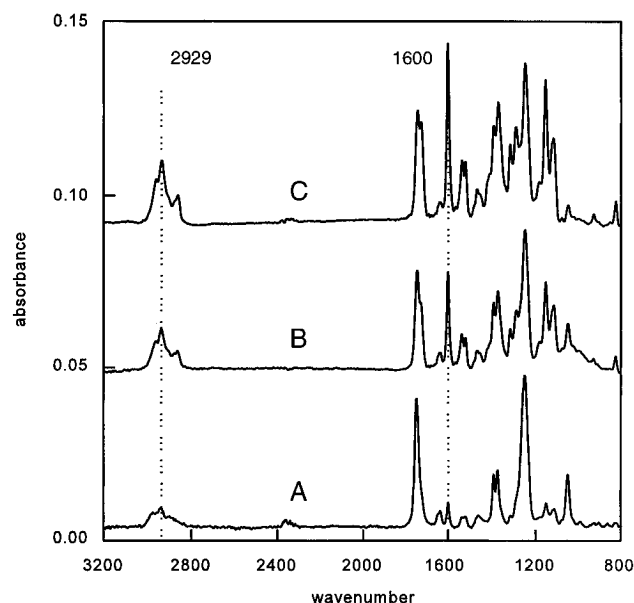


Figure 6. Grazing incidence reflection IR spectra of LB multilayers on gold of polymers (A) $13^{26.5^{74}}$, (B) $13^{60.5^{40}}$, and (C) $13^{80.5^{20}}$.

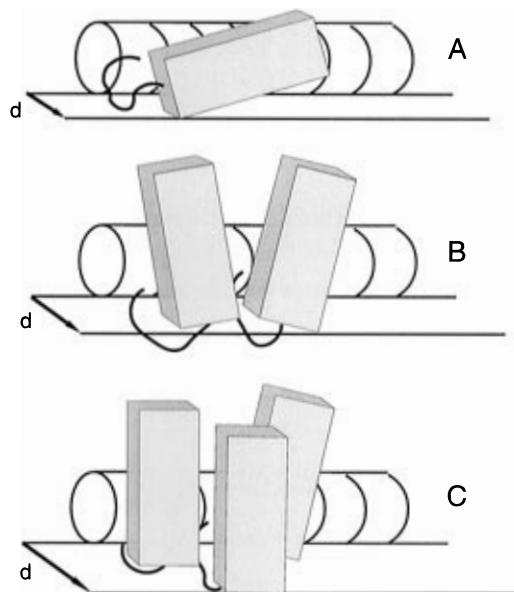


Figure 7. Orientation of the chromophores in the case of a dye content of (A) 25%, (B) 50%, and (C) 75%.

alignment: in this polymer the chromophores are almost oriented perpendicular to the LB film plane. In summary, when the dye content of the copolymers is higher, the orientation of the side groups is more perpendicular to the substrate. This result agrees with the values of the specific areas obtained from the pressure–area isotherms. The values of A_0 calculated for the chromophores decreased when the dye content of the polymers increased. This also indicates that the orientation of the side groups becomes more perpendicular to the interface when the concentration of the dye becomes larger (see Figure 7).

Figure 7A shows a schematic picture of the poly(isocyanide) backbone with one chromophore per helical turn, which corresponds to a copolymerization degree of 0.25 (comparable to polymer $13^{26.5^{74}}$). In this case the chromophore can occupy a rather large area, in agreement with the area calculated from the pressure–area isotherms (Figure 3). The orientation of the side

Table 1. Second-Order Susceptibilities of Floating Monolayers of Polymers $13^{26.5^{74}}$, $13^{60.5^{40}}$, and $13^{80.5^{20}}$

polymer	d_0^a (nm)	π (mN/m)	χ_{xxz} (10^{-9} esu)	χ_{zxx} (10^{-9} esu)	χ_{zzz} (10^{-9} esu)
$13^{26.5^{74}}$	1.4	1	4.5	7.2	16.5
		5	5.5	5.5	21.2
		15	6.2	6.2	20.5
$13^{60.5^{40}}$	2.4	1	9.3	10.7	30.1
		5	10.7	12.2	29.4
		15	16.0	15.5	50.1
$13^{80.5^{20}}$	3.8	1	8.1	9.1	21.7
		5	11.2	12.6	30.0
		15	14.6	15.5	34.4

^a The monolayer thicknesses were calculated from ellipsometric measurements on multilayered samples of the different copolymers on silicon substrates.

group is approximately random. From ellipsometry measurements the thickness per layer was calculated to be 13 Å, which is the same value as found earlier for poly((S)-1-acetoxyethylmethyl isocyanide), *i.e.*, the polymer without the chromophores.¹³

Figure 7B shows the same poly(isocyanide) backbone but now with two chromophores per helical turn, corresponding to a copolymerization degree of 0.5 (comparable to polymer $13^{60.5^{40}}$). The chromophores are forced to orient themselves as the area which is available for a single chromophore is smaller than in the case of polymer $13^{26.5^{74}}$. The thickness per layer as determined by ellipsometry, *viz.*, 2.4 nm, has increased, which is in line with a more perpendicular arrangement of the side chains. Because of the irregular structure of the top of the film, the transfer properties of this polymer are worse compared to those of polymer $13^{26.5^{74}}$.

In Figure 7C the poly(isocyanide) backbone with three chromophores per helical turn is depicted. The degree of copolymerization is 0.75, which is comparable to polymer $13^{80.5^{20}}$. Now, the area occupied by a single chromophore is even smaller than in the case of polymer $13^{60.5^{40}}$ resulting in a slightly better orientation of the chromophores. The area per repeating unit, which is proportional to the distance d (see Figure 7), has increased on increasing the local dye concentration. The observed increase of the areas in the pressure–area isotherms is in line with this. The layer thickness has further increased, namely, from 2.4 to 3.8 nm.

Nonlinear Optics. Floating Monolayers. Using the setup described by S'heeren et al.,¹⁶ values for the second-order susceptibility were determined for floating monolayers of the copolymers $13^{26.5^{74}}$, $13^{60.5^{40}}$, and $13^{80.5^{20}}$. The measurements were started after the Langmuir layers had been compressed to the desired surface pressures and after the film area had become constant. The results are compiled in Table 1. The values for χ_{xxz} and χ_{zxx} are the same within experimental error (25%), for each of the polymers at a given surface pressure. This indicates that the chromophores are all oriented in the same direction, which means that the spacer group has efficiently decoupled the motions of the chromophoric side group from those of the rigid backbone. Interestingly, the χ_{zzz} values of the copolymers $13^{60.5^{40}}$ and $13^{80.5^{20}}$ are significantly higher than those of copolymer $13^{26.5^{74}}$. As a perpendicular orientation is strongly reflected in χ_{zzz} , we may conclude that in polymers $13^{60.5^{40}}$ and $13^{80.5^{20}}$ the chromophores are more perpendicular to the water surface than in polymer $13^{26.5^{74}}$.

This result is in line with the experiments described in the former sections. As depicted in Figure 7 the side groups of polymer $13^{26.5^{74}}$ have more space available

than those of polymers **13⁶⁰·5⁴⁰** and **13⁸⁰·5²⁰**, which gives rise to a more or less random orientation in the former polymer.

LB Multilayers. Immediately after preparation, the LB multilayers of polymer **13²⁶·5⁷⁴** on glass substrates showed second-harmonic generation. The signal was, however, not stable in time and disappeared completely after storage of the samples at room temperature for a few days. Probably due to orientational reorganization of the chromophores, the polar order is completely destroyed, allowing the samples to adopt a centrosymmetrical structure. As polymer **13²⁶·5⁷⁴** has a low glass transition temperature (T_g 20 °C), such a reorganization is likely to occur.

Since LB films of polymers **13⁶⁰·5⁴⁰** and **13⁸⁰·5²⁰** have a more or less Y-type structure, the samples of these polymers are not expected to generate much second-harmonic light. Indeed no NLO activity could be detected. It would be of interest to prepare from these copolymers films that have an alternated layer structure. Such LB films may be expected to display high second-order nonlinear optical properties. Further research will be directed along this line.

Conclusions

The studies described here indicate that incorporation of spacer groups between the NLO functions in the polymer side chains and the polymer backbone leads to the formation of stable monolayers. Probably, the hydrophilic ester functions in the side chains become more accessible for interaction with the water subphase. The stable monolayers can be transferred onto substrates to yield approximately Y-type LB films. In the case of a polymer with a low dye content a perfectly Z-type LB film can be obtained. The stability of the floating monolayers increases with decreasing dye content of the copolymers. IR measurements on LB multilayers reveal a perpendicular orientation of the chromophores with respect to the plane of the film. This

orientation is more pronounced if the dye content in the polymers is higher. We may conclude that the spacer group indeed decouples the movements of the chromophore from the backbone as was expected.

Supporting Information Available: Experimental details of the synthesis of the precursors and the polymers used in this study (6 pages). Ordering information is given on any current masthead page.

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MA951203O